5 Symmetry

5.1 Rotation Operators

Consider a scalar field $f(\underline{r})$.

Example 1: The temperature at point $\underline{r}$

After a rotation of the coordinate system, the same field is described by the new function $f'(\underline{r}')$, with

$$\underline{r}' = R\underline{r} \tag{5.1}$$

Here the operator R acts on the coordinates. Introduce now the operator P_R, which acts on the function f in Hilbert space, making it follow the rotation of the coordinate system:

$$f'(\underline{r}') = P_R f(\underline{r}') = f(\underline{r}) \tag{5.2}$$

Active interpretation: In the left-hand equation, $f'(\underline{r}') = P_R f(\underline{r}')$, the operator P_R changes the function f into f'.

Passive interpretation: In the right-hand equation, rewritten as $f(\underline{r}') = P_R^{-1} f(\underline{r})$, the operator does not change the function but acts on the coordinates $\underline{r}$, changing them to $\underline{r}'$

Example 2: Let $f(\phi) = \mathrm{e}^{\mathrm{i}m\phi}$ and $R\phi = \phi' = \phi - \alpha$, a positive rotation through α:

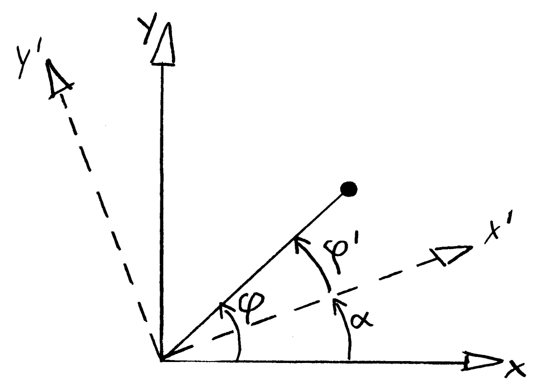

Figure 5.1: Positive rotation through α

Then

$$\underbrace{\mathrm{e}^{im(\phi'+\alpha)}}_{f'(\phi')} = \underbrace{\mathrm{e}^{im\alpha}}_{P_R}\underbrace{\mathrm{e}^{im\phi'}}_{f(\phi')} = \underbrace{\mathrm{e}^{im\phi}}_{f(\phi)} \tag{5.3}$$

5.1.1 The Euler Angles

Consider a right-handed coordinate system $\mathbf{O}xyz$ and positive rotations (like in fig. (5.1), R_z pushing a right-handed screw towards $+z$). Introduce the rotations

(i) Rotation $R_z(\alpha)$ through α around $\mathbf{O}_z$ ($\mathbf{O}_y \to \mathbf{O}_{y'}$)
(ii) Rotation $R_{y'}(\beta)$ through β around $\mathbf{O}_{y'}$ ($\mathbf{O}_z \to \mathbf{O}_{z''}$)
(iii) Rotation $R_{z''}(\gamma)$ through γ around $\mathbf{O}_{z''}$($\mathbf{O}_{y'} = \mathbf{O}_{y''} \to \mathbf{O}_{y'''}$)

Then eq. (5.3) $\Rightarrow$ (replacing m by the operator j_z)

$$f'(\underline{r}') = \mathrm{e}^{\mathrm{i}\alpha j_{z'}} f(\underline{r}') \tag{5.4}$$

$$\begin{aligned} f''(\underline{r}'') &= \mathrm{e}^{\mathrm{i}\beta j_{y''}} f'(\underline{r}') \\ &= \mathrm{e}^{\mathrm{i}\beta j_{y''}}\mathrm{e}^{\mathrm{i}\alpha j_{z''}} f(\underline{r}'') \end{aligned} \tag{5.5}$$

$$\begin{aligned} f'''(\underline{r}''') &= \mathrm{e}^{\mathrm{i}\gamma j_{z'''}} f''(\underline{r}'') \\ &= \mathrm{e}^{\mathrm{i}\gamma j_{z'''}}\mathrm{e}^{\mathrm{i}\beta j_{y'''}}\mathrm{e}^{\mathrm{i}\alpha j_{z'''}} f''(\underline{r}''') \end{aligned} \tag{5.6}$$

in the *active interpretation* using *temporary coordinates* $\mathbf{O}_z$, $\mathbf{O}'_y$.

The P_R operator of the type (5.2)-(5.3) becomes

$$P_R(\alpha\beta\gamma) = \mathrm{e}^{\mathrm{i}\gamma j_z}\mathrm{e}^{\mathrm{i}\beta j_y}\mathrm{e}^{\mathrm{i}\alpha j_z} \tag{5.7}$$

With this operator, the same coordinates must be used on both sides.

If fixed rotation axes, $\mathbf{O}xyz$, are used, one should replace $(\gamma\beta\alpha)$ by $(\alpha\beta\gamma)$ in the operator P_R.

Rotations	Axes	Operations		
		1.(z)	2.(y)	3.(z)
Active	Fixed	γ	β	α
Active	Temporary	α	β	γ
Passive	Fixed	$-\alpha$	$-\beta$	$-\gamma$
Passive	Temporary	$-\gamma$	$-\beta$	$-\alpha$

5.1.2 Rotation of Spherical Harmonics.

In the *active, temporary* picture, the rotated function becomes

$$Z'(\vartheta'\phi') = \mathrm{e}^{-\mathrm{i}\gamma j_{z'}}\mathrm{e}^{\mathrm{i}\beta j_{y'}}\mathrm{e}^{\mathrm{i}\alpha j_{z'}}\mathrm{Y}_{lm}(\vartheta'\phi') \tag{5.8}$$

In the *passive, temporary* representation

$$\begin{aligned}\mathrm{Y}_{lm}(\vartheta'\phi') &= \mathrm{e}^{-\mathrm{i}\alpha j_z}\mathrm{e}^{-\mathrm{i}\beta j_y}\mathrm{e}^{-\mathrm{i}\gamma j_z}\mathrm{Y}_{lm}(\vartheta\phi)\\ &\equiv \sum_{m'}\mathrm{D}^{l}_{m'm}(\alpha\beta\gamma)\mathrm{Y}_{lm'}(\vartheta\phi)\end{aligned} \tag{5.9}$$

Here the *rotation matrices* (***Wigner*** *matrices*)

$$\mathrm{D}^{l}_{m'm} = \langle lm'|\mathrm{e}^{-\mathrm{i}\alpha j_z}\mathrm{e}^{-\mathrm{i}\beta j_y}\mathrm{e}^{-\mathrm{i}\gamma j h_z}|lm\rangle \tag{5.10}$$

The temporary rotations $1.\alpha$, $2.\beta$, $3.\gamma$ bring $\mathbf{O}xyz$ to $\mathbf{O}x'y'z'$.

5.1.3 Rotation of $|jm\rangle$ Functions

Because the $|jm\rangle$ functions, with half-integer j, obey the same commutation rules as those with integer j, we may simply substitute l for j:

$$P_R^{-1}|jm\rangle = \sum_{m'}\mathrm{D}^{j}_{m'm}(\alpha\beta\gamma)|jm'\rangle \tag{5.11}$$

5.1.4 The 2-to-1 Homomorphism from $SU(2)$ to $SO(3)$

The ***special unitary*** *group,* $SU(2)$, consists of all unitary ($\mathbf{U}^\dagger = \mathbf{U}^{-1}$), unimodular ($\det\mathbf{U} = 1$) 2×2 matrices. We may regard it as the group of all three-dimensional rotations, spanned by the spin vectors

$$\begin{cases}\eta_1 = \alpha = |\frac{1}{2}\,\frac{1}{2}\rangle\\ \eta_2 = \beta = |\frac{1}{2}\,\text{-}\frac{1}{2}\rangle\end{cases} \tag{5.12}$$

A Pauli matrix σ_i transforms under the rotation $\mathbf{U}$ to

$$\mathbf{U}\sigma_i\mathbf{U}^\dagger = \sum_{j}^{x,y,z}\sigma_j\mathbf{A}_{ji} \tag{5.13}$$

The matrix $\mathbf{A}$ is real, orthogonal ($\mathbf{A}^\dagger\mathbf{A} = 1$) and unimodular and belongs hence to the ***special orthogonal*** *group* $SO(3)$ (consisting of 3×3 matrices), isomorphic to the group $R(3)$ of all three-dimensional rotations.

$$Rm_iR^\dagger = \sum_j m_j\mathbf{A}_{ji} \tag{5.14}$$

where the vectors m_j form a cartesian basis.

Consider now two elements, $\mathbf{U}$ and $\mathbf{V}$, of $SU(2)$ and two elements, $\mathbf{A}$ and $\mathbf{B}$, of $SO(3)$, $\to R(\mathbf{A})$ and $R(\mathbf{B})$. A comparison of (5.13) and (5.14) yields the mapping

$$\mathbf{U} \to \mathbf{A} \tag{5.15}$$

Letting $\mathbf{V} \to \mathbf{B}$, (5.13) $\Rightarrow$

$$(\mathbf{U}\mathbf{V})\sigma_i(\mathbf{V}^\dagger\mathbf{U}^\dagger) = \mathbf{U}\sigma_j\mathbf{B}_{ji} \tag{5.16}$$

Hence (5.15) is a homomorphism. In particular, as

$$\mathbf{U}\sigma_i\mathbf{U}^\dagger = (-\mathbf{U})\sigma_i(-\mathbf{U})^\dagger = \sigma_j\mathbf{A}_{ji} \Rightarrow \pm\mathbf{U} \to \mathbf{A}, \tag{5.17}$$

it is a 2-to-1 homomorphism, exactly two elements of $SU(2)$ is mapped to exactly one element of $SO(3)$.

As the angular momentum $\underline{j} = \underline{\sigma}/2$ for $SU(2)$, the matrix operator for a rotation through ϕ around $\underline{n}$ becomes (recall (5.3)):

$$\mathbf{U}(\underline{n}, \phi) = \mathrm{e}^{\mathrm{i}(\underline{\sigma}\cdot\underline{n})\phi/2} = \cos\frac{\phi}{2} + \mathrm{i}(\underline{\sigma}\cdot\underline{n})\sin\frac{\phi}{2} \tag{5.18}$$

Hence

$$\mathbf{U}(\underline{n}, 2\pi) = -\underline{\underline{\mathbf{1}}} \tag{5.19}$$
$$\mathbf{U}(\underline{n}, 4\pi) = \underline{\underline{\mathbf{1}}} \tag{5.20}$$

5.2 Double Groups

5.2.1 Non-relativistic Case with Spin

Let G be the non-relativistic or *simple* group. Its elements, like the pure rotations, R_i, commute with $\mathbf{H}$,

$$[\mathbf{H}, R_i] = 0 \tag{5.21}$$

The spin space is entirely decoupled from coordinate space. The total symmetry group is the direct product

$$G_{\text{full}} = G \times SU(2) \tag{5.22}$$

For a Coulomb potential, G_{full} is larger still (**Fock** (1936)).

5.2.2 Relativistic Case

Now the space and spin variables are coupled. Only those $\mathbf{U}_i \in SU(2)$ which correspond to an $\mathbf{R}_i$ (by (5.15)) can be included in

$$G^* = \{\pm\mathbf{R}_i\mathbf{U}_i\} \subset G \times SU(2) \tag{5.23}$$

The two signs correspond to those of (5.17). Let K be the set of all such $\mathbf{U}_i$:

$$K = \{\pm\mathbf{U}_i | \mathbf{U} \to \mathbf{R}_i\} \tag{5.24}$$

K and G^* are isomorphic, $K \cong G^*$. The relations between the four groups are seen in figure (5.2).

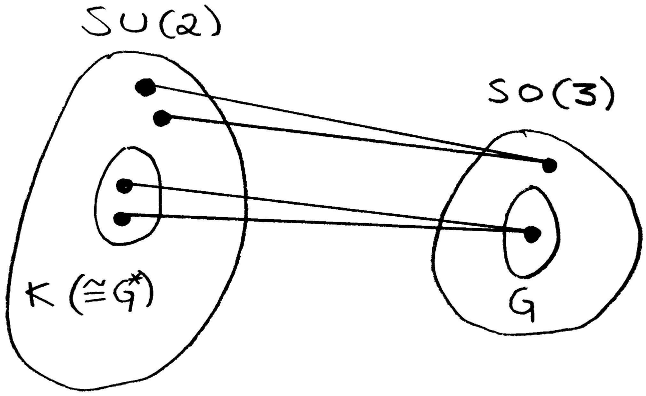

Figure 5.2: Group relations

5.2.3 Improper Rotations

The improper groups, G', are either direct products

$$G' = G \times C_i \tag{5.25}$$

where $C_i = \{E, I\}$ contains the inversion, I, or isomorphic to G. In the first case G' contains I.

Example 3:

$$T_{\mathrm{h}} = T \times C_i = \{E, 3C_2, 4C_3, 3C_3^{-1}\}\mathbf{U}\{I, 3\sigma, 4S_6^{-1}, 4S_6\} \tag{5.26}$$

5.2.4 The Group $O(3)$

All improper groups, G', are subgroups of the group $O(3)$, which is obtained from $SO(3)$ by adding the improper rotation with $\det \mathbf{A} = \pm 1$.

If the inversion is included, it commutes with all other elements, $\begin{pmatrix} -1 & & \\ & -1 & \\ & & -1 \end{pmatrix}$ being a multiple of $I = \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix}$.

5.2.5 The Double Group is a Symmetry Group of the Dirac Equation.

Consider

$$h_{\mathrm{D}} = c\underline{\alpha} \cdot \underline{p} + \beta mc^2 + V \tag{5.27}$$

with

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{pmatrix} \tag{5.28}$$

and define the transformation matrix for the i^{th} rotation as

$$\mathbf{U}_i^{\mathrm{D}} = \begin{pmatrix} \mathbf{U}_i & 0 \\ 0 & \mathbf{U}_i \end{pmatrix} \tag{5.29}$$

Consider the group

$$G_{\mathrm{D}}^* = \{\pm \mathbf{R}_i \mathbf{U}_i^{\mathrm{D}}\} \cong G^* \tag{5.30}$$

This rotation transforms the kinetic energy to

$$\begin{aligned}(\mathbf{R}_i \mathbf{U}_i^{\mathrm{D}})\underline{\alpha} \cdot \underline{p}(\mathbf{R}_i \mathbf{U}_i^{\mathrm{D}})^\dagger &= \begin{pmatrix} 0 & \mathbf{U}\sigma_k \mathbf{U}^\dagger \\ \mathbf{U}\sigma_k \mathbf{U}^\dagger & 0 \end{pmatrix} \mathbf{R} p_k \mathbf{R}^\dagger \\ &= \alpha_l p_m \mathbf{A}_{lk} \mathbf{A}_{mk} = \alpha_m p_m = \underline{\alpha} \cdot \underline{p}\end{aligned} \tag{5.31}$$

Thus the kinetic energy remains invariant under the double group operations.

5.2.6 The Element $\bar{E}$

Bethe (1929) arrived at the double-group concept by including in the group the new element $\bar{E}$, corresponding to rotations through 2π, for which

$$\bar{E}^2 = E \tag{5.32}$$

Example 4:

$$C_2 = \{E, C_2\}, \quad C_2^* = \{E, C_2, \bar{E}, \bar{C}_2 = \bar{E}C_2\} \tag{5.33}$$

In general

$$\bar{A} = \bar{E}A \tag{5.34}$$

5.2.7 Elements of Double Groups

In the multiplication table of a double group the new, barred, operations are mixed with the others. For rotations around the same axis

$$C_2\mathbf{R}_i = \begin{cases} \bar{\mathbf{R}}_j, & \text{for } 0 < \mathbf{R}_i < \pi \\ \mathbf{R}_j, & \text{for } -\pi < \mathbf{R}_i < 0 \end{cases} \tag{5.35}$$

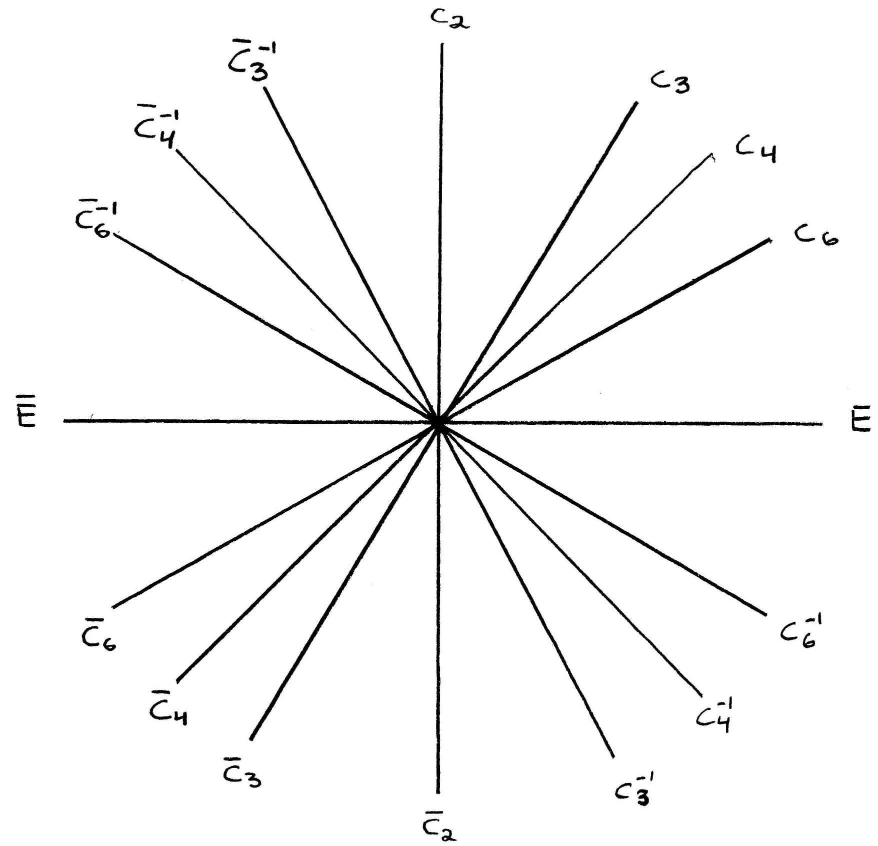

Figure 5.3: Multiplication of rotations in a double group. From **Koster** *et al.* (1963).

The properties of the inversion are

$$II = E, \quad I\bar{I} = \bar{E}, \quad \bar{I}\bar{I} = E, \quad I\mathbf{R}_i = \mathbf{S}_j, \quad I\bar{\mathbf{R}}_j = \bar{\mathbf{S}}_j \tag{5.36}$$

As

$$\sigma_{\mathrm{h}} = IC_2 \tag{5.37}$$

we get

$$\sigma_{\mathrm{h}} C_2 = IC_2^2 = I\bar{E} = \bar{I} \neq I \; ! \tag{5.38}$$

$$\sigma\sigma = (IC_2)(IC_2) = C_2^2 = \bar{E} \tag{5.39}$$

$$\sigma\bar{\sigma} = \sigma\sigma\bar{E} = \bar{E}\bar{E} = E \Rightarrow \tag{5.40}$$

$$\sigma^{-1} = \bar{\sigma} \; ! \tag{5.41}$$

Also,

$$\{E,\sigma\} \otimes \{E,\bar{E}\} = \{E,\sigma,\bar{E},\underbrace{\sigma^{-1}}_{\bar{\sigma}}\} \tag{5.42}$$

$$\sigma\sigma^{-1} = E \tag{5.43}$$

$$\sigma\bar{E} = \bar{\sigma} \tag{5.44}$$

$$\bar{E}\sigma^{-1} = \bar{E}\bar{\sigma} = \bar{E}\bar{E}\sigma = \sigma \tag{5.45}$$

For a rotation C_n,

$$C_n^n = \bar{E}, \quad C_n^{2n} = E \Rightarrow \tag{5.46}$$

$$\bar{E}C_n = C_n^n C_n = C_n C_n^n = C_n \bar{E} \tag{5.47}$$

Furthermore,

$$C_2 \mathbf{R}_i = \begin{cases} \bar{\mathbf{R}}_j, & \text{for } 0 < \mathbf{R}_i < \pi \\ \mathbf{R}_j, & \text{for} - \pi < \mathbf{R}_i < 0 \end{cases} \qquad [5.35]$$

$\Rightarrow$

$$\sigma_{\mathrm{h}} \mathbf{R}_i = IC_2 \mathbf{R}_i = \begin{cases} \bar{\mathbf{S}}_i, & \text{for } 0 < \mathbf{R}_i < \pi \\ \mathbf{S}_i, & \text{for} - \pi < \mathbf{R}_i < 0 \end{cases} \tag{5.48}$$

5.2.8 Irreducible Representations (”irreps”)

The order of the double group, $\#G^* = 2(\#G) = 2g$. Hence its irreps must satisfy

$$\sum_{i=1}^{r} n_i^2 = 2g \tag{5.49}$$

r being the number of irreps for G^*.

Example 5:

Both $C_{2\mathrm{h}}$ and $C_{2\mathrm{v}}$ have $g = 4$. They satisfy (5.49) by

$$\begin{aligned}
C_{2\mathrm{h}} &: (1^2+1^2+1^2+1^2)+(1^2+1^2+1^2+1^2) = 8 &\quad (5.50)\\
C_{2\mathrm{v}} &: (1^2+1^2+1^2+1^2)+\ 2^2 \qquad\qquad\qquad\quad = 8 &\quad (5.51)\\
&\quad\ \Gamma_1 \quad\ \ \ldots \quad\ \ \Gamma_4 \quad \Gamma_5 &
\end{aligned}$$

Thus all relativistic molecular orbitals of $C_{2\mathrm{v}}$ belong to the same irrep, Γ_5. Note that, for an even number of electrons, the *total* electronic symmetry still belongs to $\Gamma_1 - -\Gamma_4$, J being an integer (for higher symmetries, when applicable).

<u>*The reps of G are also reps of G^**</u>

We have a 2-to-1 mapping from G^* to G and a n-to-1 mapping from G to reps $\{\Gamma\}$. Thus we have a $2n$-to-1 mapping from G^* to a single matrix of the representation Γ.

The original irreps of G have basis functions, $|jm\rangle$, with integer j. For their characters

$$\chi^{(i)}(\bar{\mathbf{A}}) = \chi^{(i)}(\mathbf{A}) \tag{5.52}$$

The additional irreps of G^* have basis functions $|jm\rangle$ with *half-integer* j. For them

$$\chi^{(i)}(\bar{\mathbf{A}}) = -\chi^{(i)}(\mathbf{A}) \tag{5.53}$$

Here i is the irrep in question.

5.2.9 Classes

The number of classes equal the number of irreps,

$$k = r \tag{5.54}$$

The character of the rep, spanned by the functions $|jm\rangle$, $m = -j, \ldots, j$, becomes

$$\chi^{(j)}(\omega) = \frac{\sin(j+\frac{1}{2})\omega}{\sin\frac{1}{2}\omega} \tag{5.55}$$

For $\omega = \pi$ and half-integer j, $\chi^{(j)}(\pi) = 0$. Therefore $\chi^{(j)}(\pi + 2\pi) = -\chi^{(j)}(\pi) = 0$, as well. Thus $\chi(C_2) = \chi(\bar{C}_2) \Rightarrow C_2$ and $\bar{C}_2$ may or may not belong to the same class.

For $n \geq 2$, one always has $\chi(C_n) = -\chi(\bar{C}_n)$ and here C_n and $\bar{C}_n$ belong to different classes.

5.2.10 Theorem of Opechowski

Opechowski (1940): C_n and $\bar{C}_n$ belong to to different classes if $n \geq 2$. For $n = 2$, C_2 and $\bar{C}_2$ belong to the same class if and only if the group contains another C_2, perpendicular to the C_2 considered, or if it contains a symmetry plane, σ, containing the C_2 considered.

Similarly, S_2 and $\bar{S}_2$ belong to different classes except if there is a σ, containing the C_2 axis, or another C_2 perpendicular to it.

The reflections σ and $\bar{\sigma}$ belong to different classes, except if there exists another σ, perpendicular to it, or a C_2 in the plane σ.

Example 6:
Character table and basis functions for the group $D^*_{3\mathrm{h}}$:

$D_{3\mathrm{h}}$	E	$\bar{E}$	σ_h $\bar{\sigma}_\mathrm{h}$	$2C_3$	$2\bar{C}_3$	$2S_3$	$2\bar{S}_3$	$3C'_2$ $3\bar{C}'_2$	$3\sigma_\mathrm{v}$ $3\bar{\sigma}_\mathrm{v}$	Time inv.	Bases
Γ_1	1	1	1	1	1	1	1	1	1	a	R
Γ_2	1	1	1	1	1	1	1	-1	-1	a	S_z
Γ_3	1	1	-1	1	1	-1	-1	1	-1	a	zS_z
Γ_4	1	1	-1	1	1	-1	-1	-1	1	a	z
Γ_5	2	2	-2	-1	-1	1	1	0	0	a	$(S_x$-i$S_y)$, -$(S_x$-i$S_y)$
Γ_6	2	2	2	-1	-1	-1	-1	0	0	a	$\Gamma_3 \times \Gamma_5$
Γ_7	2	-2	0	1	-1	$\sqrt{3}$	-$\sqrt{3}$	0	0	c	$\phi(\frac{1}{2},-\frac{1}{2})$, $\phi(\frac{1}{2},\frac{1}{2})$
Γ_8	2	-2	0	1	-1	-$\sqrt{3}$	$\sqrt{3}$	0	0	c	$\Gamma_7 \times \Gamma_3$
Γ_9	2	-2	0	-2	2	0	0	0	0	c	$\phi(\frac{3}{2},-\frac{3}{2})$, $\phi(\frac{3}{2},\frac{3}{2})$

We observe that: $D_{3\mathrm{h}} = \{E; 2C_3; 3C_2; \sigma_\mathrm{h}; 2S_3; 3\sigma_\mathrm{v}\}$

a. The order of $D_{3\mathrm{h}}$ is 12. The representations Γ_7–Γ_9 satisfy (5.49) by $2^2 + 2^2 + 2^2 = 12$.

b. The elements σ_h and $\bar{\sigma}_\mathrm{h}$ belong to the same class because the C_2 axes lie in the σ_h plane. The "vertical" σ_v and $\bar{\sigma}_\mathrm{v}$ belong to the same class both because of the C_2 and because of σ_h. C_2 and $\bar{C}_2$ belong to the same class because of either σ_h or one σ_v.

c. By Opechowski's theorem, C_3 and $\bar{C}_3$ belong to different classes. So do S_3 and $\bar{S}_3$. The element $\bar{E}$ forms its own class. This gives the three classes, imposed by $k = r$, eq. (5.54).

5.3 Construction of Relativistic MO:s

5.3.1 Projection Operators

The functions ϕ^k_λ, belonging to row λ of irrep k can be projected out from an arbitrary function by using the *projection operator*

$$P^{(k)}_{\lambda\nu} = \frac{n_k}{2g}\sum_A \Gamma^{(k)}_{\lambda\nu}(A)^* \mathcal{O}_A \tag{5.56}$$

Here $g = \#G$, n_k= dimension if irrep k, $\underline{\underline{\Gamma}}^{(k)}(A)$ is the representation matrix for group element A in the irrep k and $\mathcal{O}_A$ is the symmetry operation A.

One can first operate on an arbitrary function, ψ, by $P^{(k)}_{\lambda\lambda}$ obtaining

$$\phi^k_\lambda = P^{(k)}_{\lambda\lambda}\psi \tag{5.57}$$

One then obtains the partners of ϕ^k_λ by

$$\phi^k_\nu = P^{(k)}_{\nu\lambda}\phi^k_\lambda \tag{5.58}$$

Suppose now that the basis functions in our LCAO-MO consist of atomic spinors,

$$\psi_{jlm} = \frac{1}{r}\begin{pmatrix} P(r)\chi_{jlm}(\vartheta,\phi) \\ \mathrm{i}Q(r)\chi_{j\bar{l}m}(\vartheta,\phi)\end{pmatrix} \tag{5.59}$$

The bispinors $\chi_{jlm} = |l\frac{1}{2}jm\rangle$ transform under the rotations according to $\mathrm{D}^j(\alpha\beta\gamma)$.

As noted by **Rosén** and **Ellis** (1979), then the result of the projection operator becomes

$$P^{(k)}_{\nu\lambda}\chi_{jlm} = \frac{n_k}{2g}\sum_{A=1}^{2g}\Gamma^{(k)}_{\nu\lambda}(A)^* \sum_{m'=-j}^{j}\chi_{jlm'}(-)^{l\tau_a}\mathrm{D}^j_{m'm}(\alpha\beta\gamma) \tag{5.60}$$

Here $\tau_A = 1$ if A contains the inversion operator I and $\tau_A = 0$ otherwise. Note that, outside the symmetry center, the result of $\mathcal{O}_A\psi^t_{jlm}$ may be shifted from the atom t to other, symmetry-equivalent atoms.

Example 7:
(Pyykkö and **Toivanen** 1977): Relativistic symmetry orbitals for the double group $D_{3\mathrm{h}}$. The origin is situated at the symmetry center. The variable s is +1 for $\kappa < 0$ and -1 for $\kappa > 0$.

irrep	even l	odd l
Γ_7	$\begin{cases} \lvert lj\frac{1}{2}\rangle \\ s\lvert lj\text{-}\frac{1}{2}\rangle \end{cases}$	$\begin{cases} \lvert lj\text{-}\frac{5}{2}\rangle \\ \text{-}s\lvert lj\frac{5}{2}\rangle \end{cases}$
Γ_8	$\begin{cases} \lvert lj\text{-}\frac{5}{2}\rangle \\ s\lvert lj\frac{5}{2}\rangle \end{cases}$	$\begin{cases} \lvert lj\frac{1}{2}\rangle \\ \text{-}s\lvert lj\text{-}\frac{1}{2}\rangle \end{cases}$
Γ_9	$\begin{cases} \lvert lj\frac{3}{2}\rangle \\ \text{-}s\lvert lj\text{-}\frac{3}{2}\rangle \end{cases}$	$\begin{cases} \lvert lj\text{-}\frac{3}{2}\rangle \\ s\lvert lj\frac{3}{2}\rangle \end{cases}$

Latest program: **J. Meyer** *et al.* (1996).

5.3.2 Coupling Constant Method

For the required coupling constants, see **Koster** *et al.* (1963) or **Altmann** and **Herzig** (1994). One now first constructs the non-relativistic MO:s, u^i_λ, and then couples them with the spin functions,

$$\begin{cases} \vartheta^j_{\text{-}1/2} = |\frac{1}{2}, -\frac{1}{2}\rangle = \beta \\ \vartheta^j_{1/2} = |\frac{1}{2}, \ \ \frac{1}{2}\rangle = \alpha, \end{cases} \tag{5.61}$$

using the *coupling constants* or ***Clebsch-Gordan*** *coefficients* $u^{ij,k}_{\lambda\mu,\nu}$:

$$\phi^k_\nu = \sum_{\lambda\mu} u^{ij,k}_{\lambda\mu,nu} u^i_\lambda v^j_\nu. \tag{5.62}$$

The non-relativistic funcitons u^i_λ are expressed in the $|lm_l\rangle$ representation. From that $|lm_l\frac{1}{2}m_s\rangle$ representation, (5.62), one can pass to $|l\frac{1}{2}jm_j\rangle$ representation using the Clebsch-Gordan coefficients

	j	
m_s	$l+\frac{1}{2}$	$l-\frac{1}{2}$
$\frac{1}{2}$	$\sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}$	$-\sqrt{\frac{l-m+\frac{1}{2}}{2l+1}}$
$-\frac{1}{2}$	$\sqrt{\frac{l-m+\frac{1}{2}}{2l+1}}$	$\sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}$

This method will automatically give the correct phase between the $j = l \pm \frac{1}{2}$ components.

5.4 Time Reversal

5.4.1 Non-relativistic Case

Time reversal is obtained by complex conjugating the wave function,

$$T\psi = \psi^* \equiv K\psi. \tag{5.63}$$

Let $T = K$ (complex conj.), $[H, T] = 0$.

$$\big(\mathrm{i}\hbar\frac{\partial}{\partial t}\big)\psi = H\psi \Rightarrow \big(\mathrm{i}\hbar\frac{\partial}{\partial(-t)}\big)\psi^* = T(H\psi) = H(T\psi) = H\psi^* \tag{5.64}$$

5.4.2 Inclusion of Spin

Now

$$T\psi(\underline{r}, s) = (-\mathrm{i})^{2s}\psi(\underline{r}, -s)^*. \tag{5.65}$$

This operator T is *antilinear*,

$$T(a_1\psi_1 + a_2\psi_2) = a_1^* T\psi_1 + a_2^* T\psi_2, \tag{5.66}$$

and *antiunitary*,

$$\langle T\psi_1 | T\psi_2\rangle = \langle \psi_2 | \psi_1\rangle. \tag{5.67}$$

5.4.3 n-electron Wave Functions

We now can write T as the product of (antiunitary) operator K and a unitary operator U. Possible choices are

$$T = \underbrace{\sigma_{1y}\sigma_{2y}\ldots\sigma_{ny}}_{u} K, \qquad \Big| \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \tag{5.68}$$

or

$$T\psi(\underline{r}_1, s_1, \ldots, \underline{r}_n, s_n) = (-\mathrm{i})^2(s_1 + \ldots + s_n)\psi(\underline{r}_1, -s_1, \ldots, \underline{r_n}, -s_n)^*. \tag{5.69}$$

5.4.4 Kramers' Theorem

For a system with an odd number of electrons, ψ and $T\psi$ are orthogonal.

In general, for arbitrary ψ and ϕ,

$$\begin{aligned} \langle T\psi | T\phi\rangle &= \langle UK\psi | UK\phi\rangle = \langle K\psi | K\psi\rangle = \langle \phi | \psi\rangle && (5.70) \\ \Rightarrow \langle T\psi | \psi\rangle &\overset{(5.70)}{=} \langle T\psi | T^2\psi\rangle \qquad \Big| T^2\psi = -\psi && \\ &= \langle T\psi | -\psi\rangle = -\langle T\psi | \psi\rangle = 0 && (5.71) \end{aligned}$$

Note that the equivalence used, $T^2\psi = -\psi$, only holds for an odd number of electrons!

In the absence of magnetic field, all energy levels of such systems are at least doubly degenerate.

5.4.5 The Cases (a), (b) and (c) of Wigner (1932)

Consider the representation matrices, $\underline{\underline{\Gamma}}$, of a group G^*. The operator T either does or does not give new, degenerate functions, spanning the representation matrices $\underline{\underline{\Gamma}}^*$. The following possibilities exist:

a. $\underline{\underline{\Gamma}}$ may be real.

b. $\underline{\underline{\Gamma}}$ is complex and non-equivalent to $\underline{\underline{\Gamma}}^*$

c. $\underline{\underline{\Gamma}}$ is complex and equivalent to $\underline{\underline{\Gamma}}^*$

Then:

a. The degeneracy is doubled (from n for Γ to $2n$. The functions ψ and $T\psi$ belong to the same irrep.

b. The degeneracy is doubled. If ψ spans the irrep Γ, ψ^* spans another irrep Γ^*.

c. The degeneracy remains n.

According to the ***Frobenius-Schur*** *criterion*,

$$\sum_{A=1}^{2n} \chi^{(i)}(A^2) = \begin{cases} 2g, & \text{case (a)} \\ 0, & \text{case (b)} \\ -2g, & \text{case (b)} \end{cases} \tag{5.72}$$

5.4.6 Further Examples

Some other examples of time inversion are considered below.

Momentum

$$T(\underline{p}\psi) = T\Big((-\mathrm{i}\hbar\nabla)\psi\Big) = (\mathrm{i}\hbar\nabla)\psi^2 = -(\underline{p}T\psi \tag{5.73}$$

$$T\underline{p} = -\underline{p}T, \quad \text{the sign of } \underline{p} \text{ is inverted!} \tag{5.74}$$

$$T\underline{p}T^{-1} = -\underline{p} \tag{5.75}$$

Angular momentum

$$\underline{l} = \underline{r} \times \underline{p} \qquad \Big| (5.74),\ \underline{p} \text{ changes sign under time inversion}$$

$$\Rightarrow T\underline{l} = -\underline{l}T \tag{5.76}$$

Spin-orbit Hamiltonian

$$\begin{aligned} h_{\mathrm{SO}} &= \frac{\hbar^2}{4mc^2}(\underline{\sigma}\times\nabla V)\cdot\underline{p} \quad \Big| \text{both } \underline{\sigma} \text{ and } \underline{p} \text{ change sign,} \\ &\to h_{\mathrm{SO}} \end{aligned} \tag{5.77}$$

Spin functions

$$\alpha = \begin{pmatrix}1\\0\end{pmatrix}, \quad \beta = \begin{pmatrix}0\\1\end{pmatrix}$$

$$T\alpha = (-\mathrm{i})^{2\cdot\frac{1}{2}}\beta \overset{(5.69)}{=} -\mathrm{i}\begin{pmatrix}0\\1\end{pmatrix} \tag{5.78}$$

$$T\beta = (-\mathrm{i})^{2\cdot(-\frac{1}{2})}\alpha = \ \mathrm{i}\begin{pmatrix}1\\0\end{pmatrix} \tag{5.79}$$

$$\begin{aligned} \begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} &\overset{(5.68)}{=} \mathrm{i}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}0\\ \mathrm{i}\end{pmatrix} \\ \begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} &= -\mathrm{i}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}-\mathrm{i}\\ 0\end{pmatrix} \end{aligned}$$

Rösch: $T = \begin{pmatrix}0 & -1\\ 1 & 0\end{pmatrix} \Rightarrow$

$$\begin{cases} T\alpha = \beta \\ T\beta = -\alpha \end{cases} \tag{5.80}$$

Eschrig:

$$\begin{aligned} T\Psi(\alpha) &= \begin{pmatrix} 0 & 1 & & \\ -1 & 0 & & \\ & & 0 & 1 \\ & & -1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ cp_z/A \\ c(p_x+\mathrm{i}p_y)/A \end{pmatrix}\mathrm{e}^{-\mathrm{i}\underline{p}\cdot\underline{r}} \\ &= \begin{pmatrix} 0 \\ -1 \\ -c(p_x-\mathrm{i}p_y)/A \\ cp_z/A \end{pmatrix}\mathrm{e}^{-\mathrm{i}\underline{p}\cdot\underline{r}} = -\mathrm{e}^{-\mathrm{i}\underline{p}\cdot\underline{r}}\begin{pmatrix} 0 \\ 1 \\ c(p_x-\mathrm{i}p_y)/A \\ -cp_z/A \end{pmatrix} = -\Psi(\beta) \end{aligned} \tag{5.81}$$

Compare the above with (3.45). Still, $T^2 = -\underline{\underline{1}}$

External electromagnetic fields
Invert the currents,

$$\underline{j} \to -\underline{j}, \quad \underline{A} \to -\underline{A} \tag{5.82}$$

5.5 Quaternions

For complex numbers $z = x + \mathrm{i}y = (x, y)$ both addition:

$$(x, y) + (X, Y) = (x + X, y + Y) \tag{5.83}$$

and multiplication:

$$(x, y)(X, Y) = (xX - yY, xY + yX) \tag{5.84}$$

are defined. The multiplication is

a. *commutative*, $z_1 z_2 = z_2 z_1$

b. *associative*, $a(bc) = (ab)c$

c. *norm-conserving*, $|z_1 z_2| = |z_1||z_2|$, $|z|^2 = x^2 + y^2$

Question: Can (a)-(c) be satisfied for more than two ordered components?

Answer: Hamilton and **Cayley** (1843): For *quaternions* $q = (a, b, c, d)$, with $|q|^2 = a^2 + b^2 + c^2 + d^2$, a non-commutative product with (c) can be found.